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Plastic-like moulded products made from renewable forest resources

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The bark of fast-growing wood species such as Pinus and Acacia species contains a high amount of tannin, a renewable forest resource. In this study, the possibility of utilizing radiata pine tannin as a substitute for synthetic thermosetting resins in the production of moulded products was investigated. When tannin powder and wood flour (tannin : wood flour = 1 : 1 w/w) were mixed and moulded at 190 °C and 100 MPa for 10 minutes, plastic-like moulded products with a modulus of elasticity (MOE) of 9 to 10 GPa and a modulus of rupture (MOR) of 60 to 70 MPa were obtained without further additives. Furthermore, when tannin and wood flour (1 : 1 w/w) were mixed in water and freeze-dried, tannin was partially impregnated into the wood flour, and the MOR of the moulded product increased by more than 10% compared with that of products produced without the impregnation process. The moulded products described above showed good water resistance. Moreover, an increase in wood flour content was found to upgrade the mechanical properties effectively, with a MOR of 90 to 100 MPa being obtained at 75% wood content, despite a reduction in water resistance.

1. Introduction

Various kinds of synthetic resin mouldings are derived from fossil resources such as coal and crude oil. However, these resources are not renewable and are being steadily exhausted. Therefore, production of moulded materials using renewable resources such as wood may become important in the coming century. From this perspective, the production of moulded products from radiata pine tannin was attempted since radiata pine is a fast-growing tree species cultivated extensively throughout the world, and its bark contains a significant amount of tannin, more than 30% by weight [1].

Radiata and wattle tannin which can be obtained from the barks of radiata pine and black wattle, respectively, are classified as condensed tannins. These tannins are well known to react with formaldehyde, and result in a three-dimensional network polymer. Hence, their utilization as a raw material for adhesives in the production of plywood and particleboard has been studied, and some of these substances have been used for commercial production of adhesives [2, 3]. However, the consumption of tannin for adhesives production is small and most of the bark has been disposed as waste.

Consequently, the possibility of using tannin as a raw material for moulded products was explored. The effects of moulding temperature, pressure, formaldehyde and wood flour proportions were determined, based on mechanical properties and water resistance of moulded products. Preliminary studies revealed that high strength plastic-like products comparable to phenol-formaldehyde (PF) resin moulded could be obtained by the combination of tannin and wood flour without adding any formaldehyde, hence facilitating production of these products from 100% renewable resources.

2. Experimental procedure

Radiata pine (*Pinus radiata* D. Don) bark samples were collected from the debarker of a plywood and laminated veneer lumber mill using logs from 35-year-old radiata pine trees at Mt. Gambier in South Australia. The bark samples were dried to 12% moisture content and then ground to pass through a 2.0 mm screen in a Wiley mill. The ground bark was extracted with hot (100 °C) water and the extracted solution was spray-dried. The Stiasny value of this tannin extract was 81.0% indicating that approximately 81% (tannin purity) of the extract are reactive compounds with formaldehyde. It is considered that there is a positive relationship between tannin purity and potential adhesive quality.

Radiata pine wood flour (particle sizes less than 0.16 mm) mixed with 0–8% paraformaldehyde was added to the tannin extract in a ratio of 1 to 1 (wood flour : tannin, w/w) and well mixed using a mortar and

pestle. In addition, tannin impregnated wood flour was prepared, where wood flour was added to a 5% aqueous tannin solution in a ratio of 1 to 1 (wood flour : tannin, w/w) and stirred at 40 °C for 20 hr and freeze-dried after adding various amounts of 37% formalin and stirred for a further 3 hr.

Preliminary experiments showed that hot pressing at above 190 °C and 50 MPa is required to obtain a product with a high srtrength and plastic-like appearance. Besides, there were also indications that moisture in the raw materials caused deterioration of the products when pressed at high temperature and pressure. Hence, about 15 g of oven-dried tannin and wood flour mixture, or tannin-impregnated wood flour, was put into a stainless steel cylindrical die (70 mm inner diameter) and hot-pressed at 190 °C and 100 MPa for 10 minutes, to prepare a moulded product of 2.8 mm thickness. The time to reach the designated temperature was about 2 minutes. The press was cooled to 20 °C over a period of 8 minutes, and the die at about 40 °C was removed from the press and allowed to cool to room temperature. The samples were then removed from the die. Two samples of moulded products were prepared for each combination of processing conditions. For comparison, phenol formaldehyde (PF) resin moulded products, Bakelite, were prepared, where wood flour was put into a 5% aqueous solution of low molecular PF resin (Mn of about 300, resin : wood flour = 1 : 1 by weight), freeze-dried and moulded at 160 °C and 100 MPa for 10 minutes.

Two test specimens (65.0 mm by 9.0 mm by 2.8 mm) were obtained for evaluations of mechanical properties and water resistance. The specimens were conditioned at 23 °C and 50% relative humidity for one week, prior to three-point bending test at a displacement rate of 5 mm/min and a span of 50 mm. The increments in weight and thickness after boiling for 72 hr were subsequently evaluated, based on the initial parameters under an oven-dried condition.

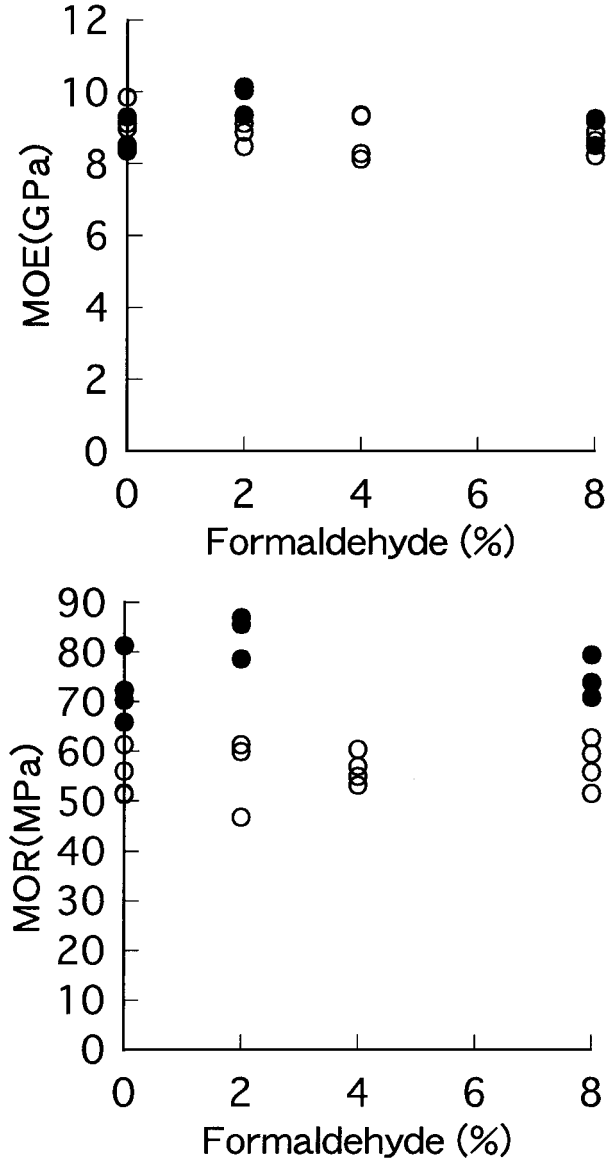

Figure 1 Effects of formaldehyde content on mechanical properties. Moulded at 190 °C and 100 MPa for 10 minutes. ○: mixture of wood flour and tannin, ●: tannin impregnated wood flour.

3. Results and discussion

3.1. Mechanical properties

3.1.1. Effects of formaldehyde content

Addition of formaldehyde is considered inevitable in the utilization of tannin as wood adhesives. In the case of wattle tannin adhesives, for example, it has been reported that the addition of 8% paraformaldehyde to the tannin is most effective for wood to wood bonding [3]. Therefore, the effects of formaldehyde content on mechanical properties of the moulded products prepared from a mixture of wood flour and tannin (1 : 1 = w/w) were first clarified.

At any formaldehyde content, plastic-like products with a density of 1.42 to 1.45 g/cm^3 were obtained. As shown in Fig. 1, where the formaldehyde content is indicated as the weight percent based on the oven-dried weight of the tannin, the modulus of elasticity (MOE) reached 9 to 10 GPa regardless of the formaldehyde level. These values were 10 to 20% higher than those of PF resin moulded products prepared for comparison. The addition of formaldehyde was also found to have no effect on the modulus of rupture (MOR) as well, in which moulded products with a MOR of more than 60 MPa were obtained.

It is worth noting that high strength moulded products could be prepared using radiata tannin without using formaldehyde as a binder. This may be due to the autocondensation of tannin, as Inoue *et al*. [4] reported that insoluble substances were produced during the extraction of tannin under high pressure and high temperature. The application of autocondensation reaction of tannins to wood adhesives has been studied and the results showed that tannins hardened in this manner yielded bonds of interior-grade particleboard [5].

3.1.2. Effects of tannin impregnation

Fig. 1 shows that tannin impregnated wood flour (wood flour : tannin=1 : 1, w/w) moulded at 190 °C and 100 MPa for 10 minutes had a MOR of 70 to 80 MPa, which is about 10 MPa higher than those of moulded products prepared from tannin and wood flour

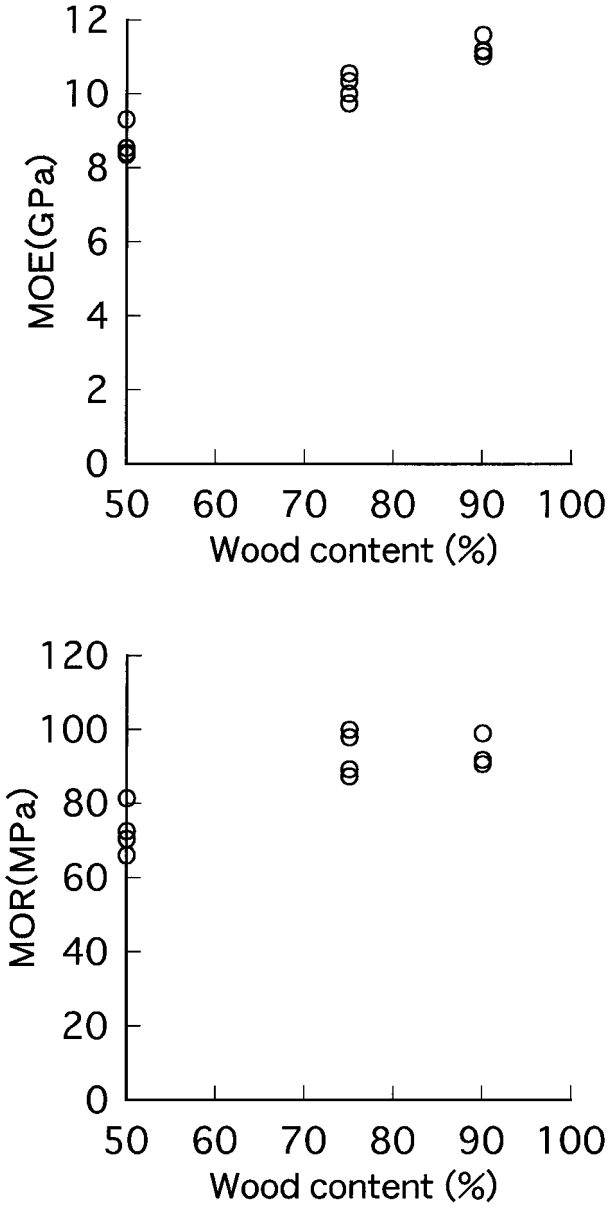

Figure 2 Effects of wood content on mechanical properties of tannin impregnated wood flour moulding. Moulded at 190°C and 100 MPa for 10 minutes.

mixture. There was no increase in MOE. When the cross-section samples (20 mm by 20 mm by 5 mm in radial, tangential, and longitudinal directions, respectively) of Sitka spruce (*Picea sitchensis*) were immersed in a 5% aqueous solution of tannin at 40 °C for one day under a vacuum condition, a 3% oven-dried volume increase was obtained, with a weight gain of 13%. This showed that part of the water soluble tannin has been retained in the cell wall. Thus, it can be seen that in products moulded from tannin impregnated wood flour, low molecular weight tannin retained between wood constituents reduced the cohesive forces between wood constituents, resulting in plasticization of the cell wall, and improved the integrity of wood flour. Since the MOR of PF moulded products lie in the range of 90 to 100 MPa, it can therefore be concluded that moulded products with mechanical properties (MOE and MOR) comparable to those of PF resin

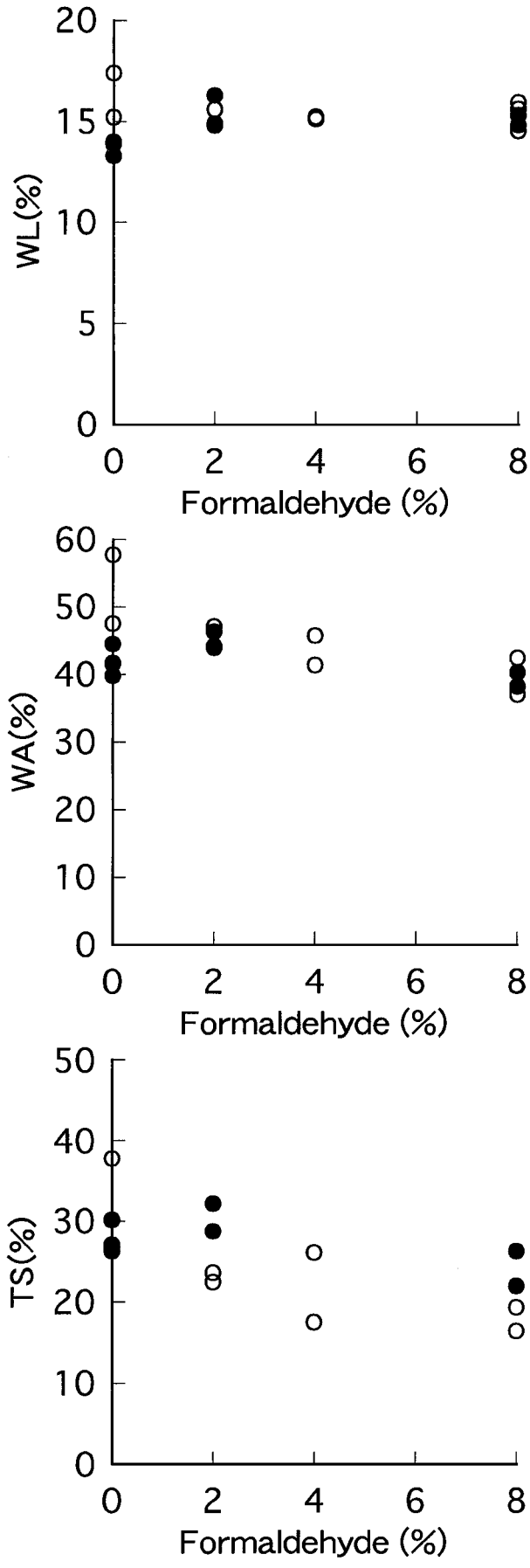

Figure 3 Effects of formaldehyde content on weight loss (WL), water absorption (WA) and thickness swelling (TS) after boiling in water for 72 hours. Moulded at 190°C and 100 MPa for 10 minutes. ○: mixture of wood flour and tanning, ●: tannin impregnated wood flour.

products could be obtained from wood flour and tannin without using any binder.

3.1.3. Effects of wood flour content

Subsequently, the effectiveness of improving the mechanical properties of the products moulded from tannin impregnated wood flour via increment of the wood flour content was investigated. A higher wood flour content was found to result in improved mechanical properties, despite giving rise to poorer flowability during moulding. As shown in Fig. 2, increasing wood flour content to 75 and 90% resulted in MOE and MOR of 9 to 11 GPa and 90 to 100 MPa, respectively. A tannin content as low as 10% is sufficient to provide a high inter-particle bond. However, since wood is a hygroscopic material, the moulded products containing 90% wood flour showed lower water resistance and large cracks were observed in the cross section after a 72-hr immersion in boiling water.

3.2. Water resistance of tannin moulded products

To use tannin moulded products as substitutes for products moulded from ordinary synthetic resin such as PF or melamine-formaldehyde, the water resistance of the products must be considered. Therefore, weight loss (WL), water absorption (WA), and thickness swelling (TS) after boiling for 72 hr were evaluated based on the oven-dried condition. The results are as shown in Fig. 3.

After the boiling test, WL of 13 to 17% was recorded, regardless of the formaldehyde content. The reduction in weight after immersion in cold water for one week was around 8 to 9%. On the other hand, WL in PF resin moulds after the boiling test was about 12%. Thus, there was no significant difference observed in the WL of tannin and PF resin moulded products.

As WL was observed due to the boiling test, WA was evaluated as changes in weights determined immediately after 72 hr of immersion in boiling water and after oven drying. As can be seen in Fig. 3, both types of moulded products registered WA of about 40%, irrespective of the formaldehyde content. The WA of the PF resin moulded products was about 20%. On the other hand, the TS of tannin moulded products decreased with an increase in formaldehyde content, and tannin moulded products added with 2% of formaldehyde demonstrated a TS comparable to that of PF resin moulded products. Furthermore, when the tannin moulded products without formaldehyde were immersed in hot water of 70 °C for 2 hours, and then in cold water of 20 °C for 1 hour, the reductions in MOE and MOR were 72.0% and 29.3%, respectively, while those in the PF resin moulded products were 29.3% and 13.0%. The results show that it is possible to obtain water resistant products by moulding tannin and wood flour alone.

4. Conclusion

The bark of fast growing tress such as Pinus and Acacia species contains a significant amount of tannin, a renewable forest resource. Despite huge accumulation, most bark is disposed as wastes at present. In this study, the utilization of tannin as a substitute for synthetic thermosetting resins for the production of moulded products was investigated. Plastic-like moulded products having mechanical properties comparable to those of PF resin moulded products and good water resistance were obtained without the addition of any formaldehyde. Therefore, tannin is a promising substitute for synthetic thermosetting resins in producing high performance plastic-like moulded products, as it is a bio-based renewable resource.

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